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ELECTROSTATIC POTENTIALS: A NEW METHOD FOR INTERPRETING AND
PREDICTING MOLECULAR REACTIVITIES AND FOR DESIGNING SYNTHETIC
PATHWAYS. APPLICATIONS TO NITROAROMATICS, NITRAMINES AND
NITRATED POLYHEDRANES.

FINAL REPORT

Peter Politzer

November 24, 1984

U. S. ARMY RESEARCH OFFICE

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I. STATEMENT OF THE PROBLEM

The general objectives of this research program have been the determination and prediction, computationally, of the reactive behavior of high-energy molecules and related species, such as intermediates in syntheses. This has involved introducing certain new concepts and techniques, as well as extending the range of applicability of older, established procedures. For instance, one of our aims was to develop a means whereby molecular electrostatic potentials, a very effective tool for elucidating electrophilic reactions, could also be applied to nucleophilic processes.

We have sought to achieve a better understanding of the basic factors that determine the reactive properties of certain important classes of high-energy molecules (including nitroaromatics and nitramines) and how these would be altered by various possible modifications of these molecules. Our efforts have also been directed toward helping to design synthetic routes to other potentially-significant classes of energetic compounds, including the nitro derivatives of strained systems such as cubane.

One of our specific aims throughout this work has been the development of a greater degree of insight into the factors governing the stabilities of the compounds of interest, and how these stabilities are affected by, for example, various substituents on the molecules. Our interests have been in both impact sensitivity and also in chemical stability, as toward moisture.

Originator furnished keywords include:

II. SUMMARY OF THE MOST IMPORTANT RESULTS

A. Development of Method for Using Electrostatic Potentials to Predict and Elucidate Nucleophilic Reactions

In the past, the electrostatic potential could not be applied as readily to the analysis of nucleophilic processes as to electrophilic ones. This is because a positive potential does not necessarily indicate a corresponding tendency to react with nucleophiles. The positive charges of atomic nuclei, being very highly concentrated, create strong positive potentials that may outweigh the negative contributions of the electrons, which are dispersed, but nevertheless may not reflect an affinity for nucleophiles.

One of our first objectives in this project was to find some means for overcoming this problem, so that nucleophilic reactions could also be subjected to this very useful mode of analysis. Our initial approach involved computing the difference between the total molecular electrostatic potential and the sum of the potentials of the individual atoms (taken to be in their free states) that comprise the molecule. It was hoped that taking this difference would eliminate the misleading contributions to the positive regions. This procedure was tested for several molecules and found to be partially successful in predicting the sites for nucleophilic attack; however it was not sufficiently consistent and conclusive to be acceptable.

Accordingly we investigated another possible approach, an adaptation of a technique that we introduced some years ago for certain types of electrophilic processes [1-3]. Rather than looking at the potential of the ground state molecule, we allow it to assume a configuration corresponding to some early intermediate stage in its reaction with a nucleophile. For an aromatic molecule, this means rotating the atom to be replaced out of the molecular plane and examining the potential in the quasi-tetrahedral fourth direction that is thereby created. For an aliphatic system, this involves, for example, computing the potential of the structure in an early phase of inversion of configuration. The key to this procedure is comparing the potentials thus obtained for the various sites or systems of interest, to determine which would be preferred by a nucleophile.

We carried out several tests of this idea, and found it to work exactly as desired [4]. For the fluorobenzene, *p*-nitrofluorobenzene pair, for instance, when each fluorine is rotated out of the ring plane, a channel of positive electrostatic potential is created, a direct pathway whereby a nucleophile can approach the fluorine position. This pathway is considerably more positive in the case of *p*-nitrofluorobenzene, in agreement with the experimental observation that the presence of an $-NO_2$ group para to a fluorine greatly increases the reactivity of the latter toward nucleophilic substitution. In another test, we applied this approach to acrolein, and were able to correctly predict that the carbonyl carbon is the most likely site for nucleophilic attack. Finally, we showed that methyl chloride is more susceptible to an S_N2 nucleophilic substitution than is methanol, again in full agreement with experimental results.

Thus the proposed procedure has been successful in all of the cases investigated. It offers the possibility, therefore, of opening a whole class of important reactions to physically meaningful interpretation and prediction.

Resulting publication:

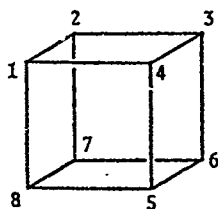
P. Politzer, S. J. Landry and T. Warnheim, "Proposed Procedure for Using Electrostatic Potentials to Predict and Interpret Nucleophilic Processes," *Journal of Physical Chemistry*, **86**, 4767 (1982).

B. Studies of the Electrostatic Potentials of Strained Systems

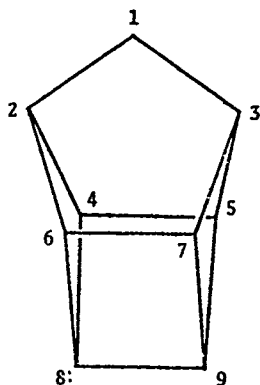
In view of the Army's very considerable interest in nitro derivatives of strained molecules as potentially useful high-energy systems, we have carried out extensive and detailed studies of the following: cyclopropane, triprismane, cubane, homocubane, *p*-bishomocubane, [1.1.1]propellane, and various mono- and polysubstituted $-\text{NO}_2$, $-\text{NH}_2$ and $-\text{CF}_3$ derivatives of these hydrocarbons. (The structures of many of the high-energy molecules to be discussed are shown on page 4.)

A very significant feature that we have found to be common to almost all of these strained hydrocarbons (one exception shall be discussed later) is a relatively strong negative electrostatic potential associated with the C-C bonds, the most negative point being near the midpoint of the bond. These indicate that the bonds in these molecules can serve as sites for electrophilic attack, which has indeed been observed in those experimental studies that have been made on these systems.

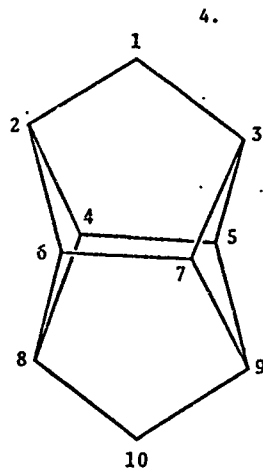
We applied our technique of rotating hydrogens away from their equilibrium positions and comparing the strengths of the resulting electrostatic potentials in the open channels of approach to the carbons that are thereby created. (Such a carbon can be regarded as being in an early stage of a substitution reaction.) We introduced this method for predicting the relative reactivities of various sites about ten years ago [2,3], and it has since been used successfully by us and by other research groups [1,4-7]. (In making our predictions, we do also take into account the relative energies required for the different hydrogen rotations.) In this manner, we were able to predict the most reactive bonds in homocubane [7] and in several isomeric bishomocubanes. The former prediction is fully confirmed by laboratory studies of rearrangement reactions



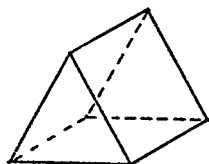
CUBANE



HOMOCUBANE



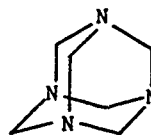
para-BISHOMOCUBANE



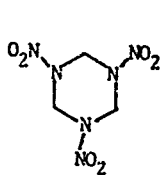
TRIPRISMANE



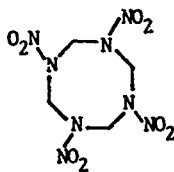
[1.1.1]PROPELLANE



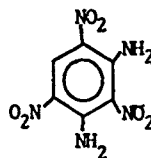
HEXAMINE



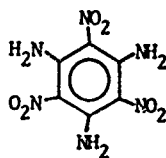
RDX



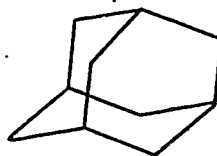
HMX



2,4-DIAMINO-1,3,5-TRINITROBENZENE
(DATB)



2,4,6-TRIAMINO-
1,3,5-TRINITROBENZENE
(TATB)



ADAMANTANE

catalyzed by metal ions. For the bishomocubanes, relative bond reactivities have not yet been determined experimentally; however we have presented our findings and predictions at several meetings sponsored by Defense Department agencies, in order to make them known to researchers working with these compounds.

The introduction of even one $-\text{NO}_2$ group has the consistent effect of eliminating the negative potentials associated with the C-C bonds in these strained hydrocarbons; this reflects the electron-withdrawing power of the nitro group. With amine substituents, the situation is similar but not as extreme; the negative C-C potentials are weakened but not eliminated [8]. The configuration of the $-\text{NH}_2$ group in the ground states of these molecules is pyramidal, $\text{>N}^{\text{H}}\text{H}$. It is interesting to note that when this group is forced to be planar, $-\text{N}^{\text{H}}_{\text{H}}$, it has the opposite effect upon the C-C potentials; they become more negative than in the parent hydrocarbon. This can be interpreted as involving a π -type charge donation by the $-\text{NH}_2$ to the carbon framework.

The preceding observations show the importance of using correct geometries, especially for amine groups. (Further examples will be given later.) Accordingly, we always carry out an extensive computational optimization of the geometry of each molecule that we study. In a number of cases, such as *p*-bis-homocubane and the various aminocubanes, there are, to our knowledge, no experimentally-determined structures. Thus we provide, by our optimizations, the only available structural data for such systems.

The electrostatic potentials of these substituted systems are also important because of what they reveal about the substituent groups themselves. We find that as the number of $-\text{NO}_2$ and $-\text{CF}_3$ groups on a given molecule increases, the strong negative potential associated with the oxygens in the former and the fluorines in the latter becomes significantly weaker. This is important relative to the stabilities, crystal packing and densities of the desired poly-substituted compounds in the solid state; all of these properties naturally depend upon repulsion between the polar substituent groups. The relevance of $-\text{CF}_3$ is that octafluoromethylcubane has been produced and studied in the solid state. Thus our comparison of $-\text{NO}_2$ and $-\text{CF}_3$ substitution will help in anticipating the possible stabilities and densities of polynitrocubanes, including octanitrocubane.

A strained molecule that has recently attracted a great deal of interest, and which shows some differences from the others that have been discussed, is [1.1.1]propellane. This hydrocarbon is considered to have a very high degree of strain, and it has the particularly notable feature that all of the bonds of the bridgehead carbons are in one hemisphere; these are the so-called "inverted" carbons (see structure I). Unlike the other strained molecules that we have

I
(inverted carbons are
indicated by arrows)



studied, the most negative electrostatic potentials in [1.1.1]propellane are not associated with the C-C bonds but rather with the bridgehead carbons. As is shown in Figure 1, there is a relatively strong negative region to the outside of each of these inverted carbons; by computing density difference plots, we confirmed that this is due to a buildup of electronic charge in each of these regions, which is accompanied by a decrease (relative to the superposed free atoms) between the bridgehead carbons. Thus we predict that the most reactive sites toward electrophiles should be to the outside of each bridgehead carbon. The available experimental data concerning the reactive behavior of [1.1.1]-propellane are in accord with this prediction [9]. We also anticipate some degree of diradical character, again focusing upon these regions by the inverted carbons.

Resulting publications:

(1) P. Politzer, L. N. Domelsmith, P. Sjöberg and J. Alster, "Electrostatic Potentials of Strained Systems: Nitrocyclopropane", *Chemical Physics Letters*, **92**, 366 (1982).

(2) P. Politzer, L. N. Domelsmith and L. Abrahamsen, "Electrostatic Potentials of Strained Systems: Cubane, Homocubane and Bishomocubane", *Journal of Physical Chemistry*, **88**, 1752 (1984).

(3) P. Politzer, K. Jayasuriya and B. A. Zilles, "Some Effects of Amine Substituents in Strained Hydrocarbons", *Journal of the American Chemical Society*, in press (1985).

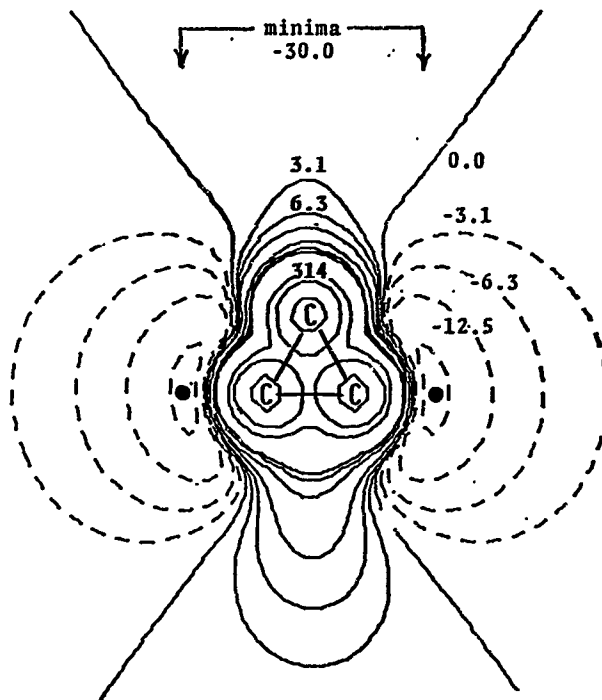


Figure 1. Calculated electrostatic potential of [1.1.1]propellane, as computed from an ab initio SCF STO-5G wave function using a geometry that had been optimized at the 6-31G* level with the GAUSSIAN 80 program. The potential is shown in the plane passing through the two bridgehead (inverted) carbons and the methylene carbon. Contour values are in kcal/mole. The positions of the most negative values of the electrostatic potential (potential minima) are indicated by the solid circles, and correspond to -30.0 kcal/mole.

C. Introduction and Applications of the Bond Deviation Index

Early in this project, we began to use the concept of "bond path", pioneered by Bader and his colleagues [10], as a means of studying chemical bonds. The bond path is the ridge of maximum electronic density that links two chemically-bonded nuclei. (In cyclopropane, for instance, the C-C bond paths curve outward, consistent with the idea of bent bonds; in propane, on the other hand, they are straight [10,11].) In order to put this on a more quantitative basis, we have introduced a new property, the "bond deviation index" [12]. This is a numerical measure of the extent to which an actual bond path deviates from a reference path defined in terms of the superposed electronic densities of the undistorted free atoms placed at the same positions as they occupy in the molecule. As examples, the bond deviation indices for the C-C bonds in propane and cyclohexane are 0.000; in cyclopropane, they are 0.080, and in tetrahedrane, 0.120 [12].

While many of our applications of this type of analysis have been to strained molecules, it is by no means limited to such systems, and we have also used it, for instance, to study the bonding in certain organophosphorus compounds. The bond deviation index represents a quantitative means of characterizing chemical bonds and allowing meaningful comparisons to be made. For example, our calculated bond deviation indices for triprismane show that its C-C bonds can be viewed as being of two types: cyclopropane-like (the bonds in the three-sided faces), and cubane-like (the bonds connecting the three-sided faces). The calculated electrostatic potentials of the triprismane C-C bonds confirmed the validity of their being classified as belonging to these two categories [8].

A key advantageous feature of the bond deviation index is that it permits one to focus specifically upon any individual bond in a molecule, rather than being obliged to deal with quantities that reflect the molecule as a whole. By means of the bond deviation index, one can observe and compare the effects of chemical substitution and structural distortion upon each individual bond in a molecule. We have now computed these indices for the bonds in about 30 molecules, and have used them in analyzing the reactive properties of these systems. For example, they were an integral part of the studies (mentioned above) of the reactive behavior of cubane, homocubane and p-bishomocubane [7].

There are also indications that the bond deviation index may provide a means for predicting when the total strain energy of a molecule is the sum of the strain energies of its component parts. For instance, as mentioned above, the indices for triprismane show that it has two cyclopropane-like and three cubane-like faces. And indeed, taking twice the strain energy of cyclopropane plus 3/6 times that of cubane (which has six faces) actually gives a result that is close to the strain energy of triprismane [13].

Resulting publication:

P. Politzer, L. Abrahamsen, P. Sjöberg and P. R. Laurence, "The Use of Bond Paths for Quantitatively Characterizing Bond Strain", Chemical Physics Letters, 102, 74 (1983).

Results and discussions of bond deviation index calculations have also been included in several others of our publications, listed elsewhere in this report.

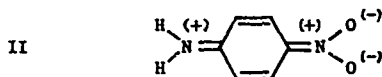
D. Studies of Nitroaromatic Systems

We have computed wave functions, structures and various properties (electrostatic potentials, electronic densities, force constants, energies, atomic charges, etc.) for about 15 mono- and disubstituted benzene derivatives. Most of these included at least one -NO_2 substituent, with -NH_2 , -CH_3 and -NO as other possibilities. We have used these results to study the effects that these substituents have upon each other and upon the overall reactivities and stabilities of the molecules.

For instance, by comparing our computed C-NO_2 stretching force constants for nitrobenzene, *m*-dinitrobenzene, and *o*- and *p*-nitroaniline, we have ascertained that the C-NO_2 bond is strengthened by the presence of an -NH_2 , particularly when the latter is in the ortho position, but is relatively unaffected by a meta- NO_2 . We have also investigated how rotation of the -NO_2 in nitrobenzene around the C-N bond affects the reactivities of various sites on the ring. While the most stable orientation for the nitro group in this molecule is in the plane of the ring, steric factors may force it to rotate out of this plane in some polysubstituted systems. This affects its conjugation with the ring, and may change the reactivities of various sites. Our preliminary conclusion is that this does occur, but that the effect is a relatively small one. The influence of the nitro group is exerted primarily inductively, and this does not involve conjugation with the ring.

The strong electron-withdrawing power of the $-\text{NO}_2$ group, which has manifested itself by eliminating the negative electrostatic potentials associated with the C-C bonds in strained hydrocarbons (see above), is now found to eliminate the negative regions above and below the aromatic ring that are present in benzene and especially in aniline, reflecting their π electrons [14]. In the case of the nitroanilines, which we have examined in particular detail, we have found that the power of the $-\text{NO}_2$ group to deactivate the aromatic ring toward electro-attack overwhelms the opposing, activating tendency of the $-\text{NH}_2$ [14]. To the extent that the nitroanilines do undergo electrophilic substitution, however, our potential plots indicate that it should be governed by the directing properties of the amine groups.

These studies again underscore the importance of geometry optimization. In aniline, we find the $-\text{NH}_2$ group to be pyramidal, in agreement with experimental determinations; in the nitroanilines, however, our optimizations show it to be planar. The strong electron-withdrawing effect of $-\text{NO}_2$ apparently causes the $-\text{NH}_2$ to adopt the planar configuration, in which it is better able to act as a π -electron donor, via increased contributions from structures such as II, in which the amine nitrogen is sp^2 -hybridized, with its hydrogens in the plane of the ring.



Resulting publication:

P. Politzer, L. Abrahmsen and P. Sjöberg, "Effects of Amino and Nitro Substituents upon the Electrostatic Potential of an Aromatic Ring", *Journal of the American Chemical Society*, **106**, 855 (1984).

E. Discovery of Positive Electrostatic Potential Buildups Near Aromatic C- NO_2 Bonds

In the course of the studies of aromatic systems described above, we have discovered that the electrostatic potentials of nitroaromatic molecules show

unexpected buildups of positive potential above and below the C-NO₂ bond regions. Their magnitudes depend upon the natures and locations of other substituents on the aromatic ring. Such effects, when not at nuclear positions, are certainly uncommon and we have accordingly investigated this in some detail in the case of nitrobenzene. On the basis of its computed electric field and also calculations of its interaction with OH⁻, we have reached the very intriguing conclusion that the C-NO₂ bond in nitrobenzene (and presumably in the other nitroaromatics as well) can serve as an initial site for nucleophilic attack. Showing the key role played by electrostatic effects in the OH⁻ interaction is the fact that we find a direct relationship between the potential of nitrobenzene at various points in the C-NO₂ region and its interaction energy with OH⁻ at those points.

Some immediate mechanistic applications of these results are in the reactions of nitroaromatic molecules with hydroxide and alkoxide ions to form Meisenheimer complexes [15], and in their reactions with hydrogen halides that are being studied by Nielsen and co-workers [16]. The ability of C-NO₂ bond regions to serve as initial sites for nucleophilic attack may well be a very significant contributing factor to whatever degrees of chemical instability are shown by various nitroaromatic molecules, as toward hydrolysis for instance.

Resulting publication:

P. Politzer, P. R. Laurence, L. Abrahmsen, B. A. Zilles and P. Sjöberg, "The Aromatic C-NO₂ Bond as a Site for Nucleophilic Attack", Chemical Physics Letters, 111, 75 (1984).

F. Mechanistic Studies of Aromatic Nitration

In order to help clarify some aspects of the mechanisms of aromatic nitrations, we have computed the structures, stabilization energies, and atomic charge redistributions associated with the formation of both weakly- and strongly-bound benzene·NO₂⁺ and toluene·NO₂⁺ complexes that are possible intermediate stages in the nitration of these aromatic molecules. The initial weakly-bound complexes are relatively delocalized, with the NO₂⁺ approximately parallel to the aromatic ring and roughly 2.8 Å above it, in a region of negative electrostatic potential. The strongly-bound complexes are localized at specific ring carbons (three isomers in the case of toluene), and can be regarded as sigma complexes.

Certain interesting and consistent patterns can be seen in our results. One of these is the fact that the same type of resonance structure appears to be the dominant contributor to each of the four sigma complexes. Another is the picture that emerges of the two functions performed by the methyl group in toluene and its complexes: First, it induces a rearrangement of charge within the aromatic ring whereby the carbon to which it is attached becomes more positive (in agreement with the ^{13}C NMR spectra of benzene and toluene), by essentially the same increment in each case. The resulting electrostatic interaction, $\text{H} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{C}^{-\delta} \text{C}^{+\delta}$, may be responsible for the various stabilization effects in the toluene- NO_2^+ sigma complexes that result in the well-known ortho, para directing properties of $-\text{CH}_3$. A second function of the methyl group, under the stimulus of the strong electron-attracting power of the $-\text{NO}_2$, is as a source of electronic charge, which comes from its hydrogens. This is observed in the weakly-bound complex as well as the strongly-bound ones.

Resulting publication:

P. Politzer, K. Jayasuriya, P. Sjöberg and P. R. Laurence, "Properties of Some Possible Intermediate Stages in the Nitration of Benzene and Toluene", *Journal of the American Chemical Society*, in press (1985).

G. Relationships for Correlating and Predicting Impact Sensitivities of Nitroaromatic Compounds

We have discovered two good correlations between the experimentally-measured impact sensitivities of a group of nitroaromatic compounds and certain electronic properties. The compounds are: 2,3,4,6-tetranitroaniline, 2,4,6-trinitrophenol, 1,3,5-trinitrobenzene, 2,4,6-trinitroaniline, 2,4,6-trinitrotoluene, 2,4-diamino-1,3,5-trinitrobenzene and 2,4,6-triamino-1,3,5-trinitrobenzene.

First, there is a direct relationship between the impact sensitivity and the positive potential at the C- NO_2 bond midpoint, V_{mid} , that can be computed from the calculated atomic charges of the carbon and nitrogen atoms [17]. (Both of these charges are generally positive.) The relationship is shown in Figure 2.

Second, there is a good correlation between impact sensitivities and the unbalanced electrostatic forces within the $-\text{NO}_2$ groups in the crystalline forms of the compounds (Figure 3). The unbalanced forces come about because the crystalline environments distort the molecules from their isolated gas-phase

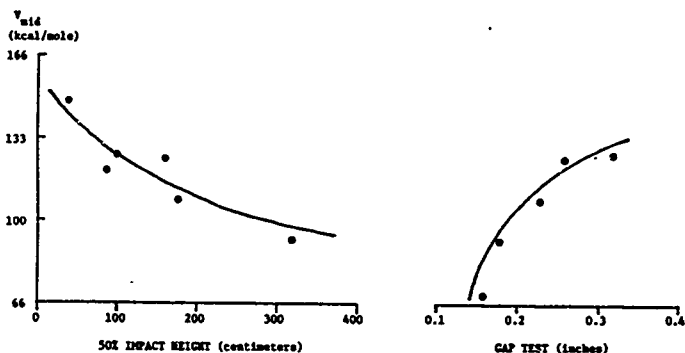


Figure 2. Correlations between two different experimental measures of impact sensitivity (50% impact height and gap test) [19] and the positive electrostatic potential at the C-NO₂ bond midpoint, V_{mid} , that can be calculated from the carbon and nitrogen atomic charges.

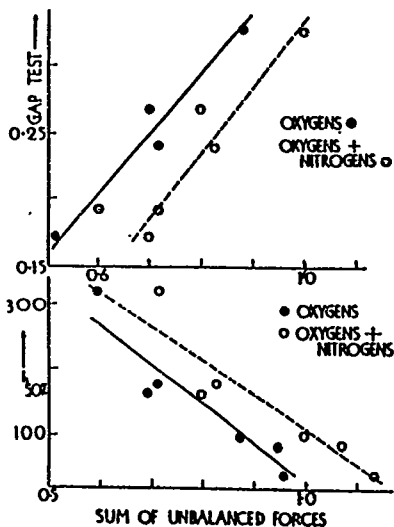


Figure 3. Correlations between two different experimental measures of impact sensitivity (gap test, in inches, and 50% impact height, in centimeters) [19] and the sum of the unbalanced intramolecular electrostatic forces upon the -NO₂ oxygens ● and upon the -NO₂ oxygens and nitrogens ○. A total of seven poly-substituted nitroaromatic molecules are included (see text).

equilibrium geometries. As a result, the net intramolecular electrostatic force upon each nucleus (due to the electrons and other nuclei in the molecule) is not zero, as it should be at equilibrium, but rather has some finite value. We calculate these forces from the molecular wave function that is computed using the molecule's geometry in the crystal. By summing the net forces that are exerted upon all of the -NO_2 oxygens in a molecule, we obtain a quantity that correlates well with the compound's measured impact sensitivity. Equally good results are produced by including the net forces upon the -NO_2 nitrogens in the summations (Figure 3).

These relationships provide insight into some of the factors that determine impact sensitivities and what consequences may be anticipated from modifications such as different functional groups. They will also allow reliable predictions to be made for compounds that have not been tested; indeed, the correlation involving V_{min} can be used in evaluating potentially important compounds that have not yet even been synthesized, since it does not require the crystalline structure.

H. Studies of Nitramines

In the course of a detailed study of nitramines, we have computed optimized structures, energies, electrostatic potentials, bond deviation indices, bond force constants, atomic charges and overlap populations for more than a dozen saturated six-membered-ring systems, containing three or fewer ring nitrogens and substituted with zero, one, or two nitro groups. Many of these structures were not previously known. The interest in these molecules is of course due to their relationship to RDX and HMX, currently two of our most effective explosives. For somewhat similar reasons, we have also computed the properties of hexamethylenetetramine (hexamine), which is a starting material in the manufacture of both RDX and HMX.

Using these results, we are analyzing the reactivities and stabilities of these systems, and how they are affected by structural modifications, such as varying the number of ring nitrogens and the number and locations of -NO_2 groups. We have been able to show, for example, that the N-N bond is stronger in dimethyl nitramine than in cyclic nitramines, which is in agreement with recent findings in laser-induced decomposition studies [18]. One of our aims in this work is to elucidate the decomposition pathways of nitramines, such as RDX and HMX.

I. Development of Method for Calculating Molecular Energy Differences from Electrostatic Potentials at Nuclei

In the course of our work with electrostatic potentials, we developed a formula that gives the difference in energy of two isoelectronic systems in terms of the electrostatic potentials at their nuclei. When tested for nine pairs of diatomic molecules and molecular ions, the average error relative to the experimental value was only 0.28%. It is particularly noteworthy that in every instance, our energy difference is more accurate than the Hartree-Fock prediction, even though our potentials were obtained from the same Hartree-Fock wave functions. An immediate application of our formula is in the calculation of molecular electron affinities, which are often quite difficult to determine experimentally. Overall good results were obtained in computing the electron affinities of C_2 , OF and CN.

Resulting publication:

P. Politzer and P. Sjöberg, "A Formula for Calculating Molecular Energy Differences from Electrostatic Potentials at Nuclei", *Journal of Chemical Physics*, 78, 7008 (1983).

III. PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS WORK

A. Publications

- (1) P. Politzer, S. J. Landry and T. Warnheim, "Proposed Procedure for Using Electrostatic Potentials to Predict and Interpret Nucleophilic Processes" *Journal of Physical Chemistry*, 86, 4767 (1982).
- (2) P. Politzer, L. N. Domelsmith, P. Sjöberg and J. Alster, "Electrostatic Potentials of Strained Systems: Nitrocyclopropane" *Chemical Physics Letters*, 92, 366 (1982).
- (3) P. Politzer and P. Sjöberg, "A Formula for Calculating Molecular Energy Differences from Electrostatic Potentials at Nuclei" *Journal of Chemical Physics*, 78, 7008 (1983).
- (4) P. Politzer, L. Abrahamsen, P. Sjöberg and P. R. Laurence, "The Use of Bond Paths for Quantitatively Characterizing Bond Strain" *Chemical Physics Letters*, 102, 74 (1983).
- (5) P. Politzer, L. N. Domelsmith and L. Abrahamsen, "Electrostatic Potentials of Strained Systems: Cubane, Homocubane and Bishomocubane" *Journal of Physical Chemistry*, 88, 1752 (1984).
- (6) P. Politzer, L. Abrahamsen and P. Sjöberg, "Effects of Amino and Nitro Substituents upon the Electrostatic Potential of an Aromatic Ring" *Journal of the American Chemical Society*, 106, 855 (1984).
- (7) P. Politzer, K. Jayasuriya and B. A. Zilles, "Some Effects of Amine Substituents in Strained Hydrocarbons" *Journal of the American Chemical Society*, in press (1985).
- (8) P. Politzer, P. R. Laurence, L. Abrahamsen, B. A. Zilles and P. Sjöberg, "The Aromatic C-NO₂ Bond as a Site for Nucleophilic Attack" *Chemical Physics Letters*, 111, 75 (1984).
- (9) P. Politzer, K. Jayasuriya, P. Sjöberg and P. R. Laurence, "Properties of Some Possible Intermediate Stages in the Nitration of Benzene and Toluene" *Journal of the American Chemical Society*, in press (1985).

B. Presentations

- (1) Seminar on High Density Energetic Materials, sponsored by U.S. Army Armament Research and Development Command, Dover, NJ, May, 1982.
- (2) Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May, 1983.
- (3) Large Caliber Weapon Systems Laboratory, U.S. Army Armament Research and Development Command, Dover, NJ, June, 1983.
- (4) Nitrations Conference, sponsored by U.S. Army Research Office, U.S. Air Force Office of Scientific Research and SRI International, Menlo Park, CA, July, 1983.
- (5) Workshop on Energetic Material Initiation Fundamentals, sponsored by U.S. Office of Naval Research, U.S. Army Research Office and U.S. Air Force Office of Scientific Research, Chestertown, MD, August, 1983.
- (6) Chemical Defense Research Conference, sponsored by the Chemical Research and Development Center, Aberdeen Proving Ground, MD, November, 1983.
- (7) Working Group Meeting on Synthesis of High Density Energetic Materials, sponsored by U.S. Army Armament, Research and Development Center, Dover, NJ, May, 1984.
- (8) Research Meeting, sponsored by U.S. Office of Naval Research, Arlington, VA, May, 1984.
- (9) Department of Chemistry, New Jersey Institute of Technology, Newark, NJ, July, 1984.
- (10) Series of three lectures, Large Caliber Weapon Systems Laboratory, U.S. Army Armament Research and Development Center, Dover, NJ, July-August, 1984.

IV. SCIENTIFIC PERSONNEL WHO PARTICIPATED IN THIS WORK

A. Research Associates

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C. Degrees Awarded

None.

V. BIBLIOGRAPHY

- [1] P. Politzer and K. C. Daiker, in: The Force Concept in Chemistry, B. M. Deb, ed., Van Nostrand-Reinhold, New York, 1981, ch. 6.
- [2] P. Politzer, R. A. Donnelly and K. C. Daiker, J. Chem. Soc., Chem. Commun., 617 (1973).
- [3] P. Politzer and H. Weinstein, Tetrahedron 31, 915 (1975).
- [4] P. Politzer, S. J. Landry and T. Warnheim, J. Phys. Chem. 86, 4767 (1982).
- [5] O. Chalvet, C. Decoret and J. Royer, Tetrahedron 32, 2927 (1976).
- [6] J. Bertran, E. Silla, R. Carbo and M. Martin, Chem. Phys. Letters 31, 267 (1975).
- [7] P. Politzer, L. N. Domelsmith and L. Abrahmsen, J. Phys. Chem. 88, 1752 (1984).
- [8] P. Politzer, K. Jayasuriya and B. A. Zilles, J. Amer. Chem. Soc., in press (1985).

- [9] W. D. Stohrer and R. Hoffmann, J. Amer. Chem. Soc. 94, 779 (1972);
K. B. Wiberg and F. H. Walker, J. Amer. Chem. Soc. 104, 5239 (1982).
- [10] R. F. W. Bader, T.-H. Tang, Y. Tal and F. W. Biegler-König, J. Amer. Chem. Soc. 104, 940, 946 (1982).
- [11] P. Politzer, L. N. Domelsmith, P. Sjöberg and J. Alster, Chem. Phys. Letters 92, 366 (1982).
- [12] P. Politzer, L. Abrahmsen, P. Sjöberg and P. R. Laurence, Chem. Phys. Letters 102, 74 (1983).
- [13] J. F. Liebman and A. Greenberg, Chem. Revs. 76, 311 (1976).
- [14] P. Politzer, L. Abrahmsen and P. Sjöberg, J. Amer. Chem. Soc. 106, 855 (1984).
- [15] M. R. Crampton and P. M. Wilson, J. Chem. Soc. Perkin II, 1854 (1980);
B. Gibson and M. R. Crampton, *ibid.*, 648 (1979).
- [16] A. T. Nielsen, A. P. Chafin and S. L. Christian, J. Org. Chem., in press.
- [17] F. J. Owens and P. Politzer, in preparation.
- [18] C. Capellos, private communication.
- [19] M. J. Kamlet and H. G. Adolph, Propellants & Explosives 4, 30 (1979);
F. J. Owens, private communication.